

Determination of the Saturation Adsorption of Surfactant in Polymer Latices

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ABSTRACT: The volumetric determination of the surfactant adsorption density at maximum packing (saturation) is studied in binary latex blends. A phenomenological description for latex mixtures that are not free of surfactant prior to titration predicts a quadratic dependence for the saturation adsorption density as a function of the fractional surface area of the latex compounds. The expected behavior was verified experimentally from conductometric titrations of sodium dodecyl sulfate in blends of homopolymer latices cleaned with the serum replacement technique. Accord-

ingly, it is shown that surfactant titration of binary latex blends provides indications about the level of cleaning of the mixed compounds. Furthermore, when latex mixtures are prepared by using a surfactant-free reference latex, this approach may be used for the estimation of the saturation adsorption area of the bare polymer surface for an incompletely cleaned latex. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3226–3230, 2004

Key words: Adsorption; dispersions; latices; surfactant

INTRODUCTION

Since its original introduction by Maron et al.¹ as a volumetric method for the estimation of the specific surface area of dispersed polymer colloids, surfactant (or soap) titration has been successfully applied for the determination of the molecular adsorption area of surfactants at the polymer/water interface in polymer latices.^{2–7} At maximum packing (saturation), the surfactant adsorption area of polymer colloids depends, among other factors, on the nature of the polymer at the particle surface and, hence, reveals some characteristics of the particle structure.^{4,6–8} Tensiometric and conductometric measurements were widely reported for the monitoring of surfactant titrations. When compared to surface tension, conductivity measurements are particularly convenient for the continuous monitoring of ionic surfactant titrations.⁷ For a proper determination of the saturation adsorption densities, preparative latex cleaning is required to remove tensioactive agents and electrolytes used during synthesis or formulation. This critical cleaning step leads to systematic errors if not controlled carefully.

In this article, conductometric surfactant titrations of binary latex blends are considered more closely. In particular, the determination of the saturation adsorption area is investigated for latex mixtures containing residual surfactant prior to titration. It is shown that

surfactant titrations of a binary latex blend (1) can provide indications about the level of cleaning of the mixed compounds and (2) may be used for the estimation of the saturation adsorption area of the bare polymer surface of an incompletely cleaned latex, particularly when carried out in combination with a suitable reference latex.

EXPERIMENTAL

Latex synthesis

Homopolymer latices of polystyrene (PS), poly(*n*-butyl acrylate) (PBA), and poly(methyl methacrylate) (PMMA) (UCB, Drogenbos, Belgium) were prepared according to a conventional semibatch emulsion polymerisation process^{9,10} described elsewhere in more detail.⁸ Sodium dodecyl sulfate (SDS) was used as emulsifier and the amount of initiator (≈ 0.06 wt % ammonium persulfate) was kept at a low level. The final dry solid content of the latices was typically ≈ 20 wt %. An additional PMMA latex (PMMA') was prepared without emulsifier by using ≈ 0.03 wt % ammonium persulfate as initiator. Here, a stable polymer emulsion could be obtained for a polymer content of ≈ 10 wt %.

Sample preparation and characterization

Prior to titration, the latices (except PMMA') were diluted to approximately 4–6 wt % solids and cleaned by serum replacement to remove surfactant and electrolyte remaining from their preparation. The latex was charged in a 400-cm³ ultrafiltration cell with a

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TABLE I
Latex Characteristics

Latex	d (nm)
PS	178
PBA	120
PMMA	109
PMMA'	419

polycarbonate filtration membrane (pore size, 100 nm; Osmotics). Distilled deionized water (conductivity $\approx 1 \mu\text{S}/\text{cm}$) was fed to the cell and the filtrate was collected. The degree of latex cleaning was varied by using different cleaning periods ranging from 1 day to more than 2 weeks.

The hydrodynamic particle size d (z-average) of the cleaned latices was measured by photon correlation spectroscopy by using a Malvern Lo-C Autosizer with an 8-bit autocorrelator. The polydispersity index, derived from a cumulants analysis of the time autocorrelation function of the scattered light intensity,¹¹ was better than 0.05, suggesting narrow particle size distributions for the studied latices. The particle size characteristics of the homopolymer latices are displayed in Table I. The dry solid content of the latices was determined gravimetrically.

The conductometric titrations were carried out at room temperature ($22 \pm 1^\circ\text{C}$) by using an automatic titroprocessor (Metrohm, 716 DMS Titrino) and a conductometer (Metrohm, 712). A 0.1M titrant solution of SDS (99% purity, Sigma) was added stepwise (every 12 s) in volume increments of $20 \mu\text{l}$ to $\approx 30 \text{ g}$ of sample while stirring to establish equilibrium.

RESULTS AND DISCUSSION

Figure 1 shows a typical conductometric SDS titration of distilled deionized water and a cleaned PS latex. The SDS concentration where the slope of the titration curve decreases corresponds to the saturation point where micelles start to form [i.e., the critical micelle concentration (cmc)]. Because of adsorption of surfactant onto the polymer particles, the cmc of a latex shifts toward higher values with respect to water. At maximum packing of surfactant at a polymer/water interface, the saturation adsorption density σ can be estimated from the volumetric data as

$$\sigma = \frac{n_a}{S_p} \cong \frac{n^{\text{add}} - n_w}{m_p A_{\text{sp}}} \quad (1)$$

where n^{add} denotes the total number of surfactant molecules added at the break point of the titration, n_a is the amount of surfactant adsorbed onto the available polymer surface of area S_p , and n_w is the total amount residing in the aqueous phase at saturation.

As established previously, n_w can be determined from the cmc value of the surfactant in water.² For SDS, a cmc value of $8.22 \pm 0.04 \text{ mmol}/\text{L}$ was determined at 22°C .⁸ S_p can be calculated from the polymer mass m_p in the sample and the specific surface area A_{sp} of the particles. In the assumption of uniform spherical particles, A_{sp} can readily be estimated from the average hydrodynamic particle diameter d by

$$A_{\text{sp}} = \frac{6}{\rho d} \quad (2)$$

where ρ is the particle density. The reciprocal value of the adsorption density yields the molecular adsorption area (i.e., $a_s = 1/\sigma$).

It is noticed that the equality in eq. (1) is satisfied if the polymer latex is completely free of surfactant before titration. If not, two approximations are introduced by using eq. (1). First, the numerator on the right-hand side of eq. (1) is $n^{\text{add}} - n_w = n_a^{\text{add}} - n_w^{\text{in}}$ and provides an estimation of the added amount of surfactant n_a^{add} adsorbed on the particles only when the initial amount of surfactant in the aqueous phase n_w^{in} can be neglected (i.e., $n_w^{\text{in}} \ll n_a^{\text{add}}$). This was assumed throughout this study. Second, the estimated quantity n_a^{add} differs from the maximum value n_a by the initial amount of surfactant n_a^{in} as it returns the excess amount of surfactant required to maximally cover the particle surface (i.e., $n_a^{\text{add}} = n_a - n_a^{\text{in}}$). The latter is illustrated in Table II where the saturation adsorption densities and molecular adsorption areas of SDS are shown for the investigated latices after various cleaning periods. As expected, for increasing cleaning times, higher adsorption densities are found due to the progressive removal of surfactant and, hence, the decrease of n_a^{in} . From a comparison of the adsorption density for the PMMA and PMMA' latex, respectively,

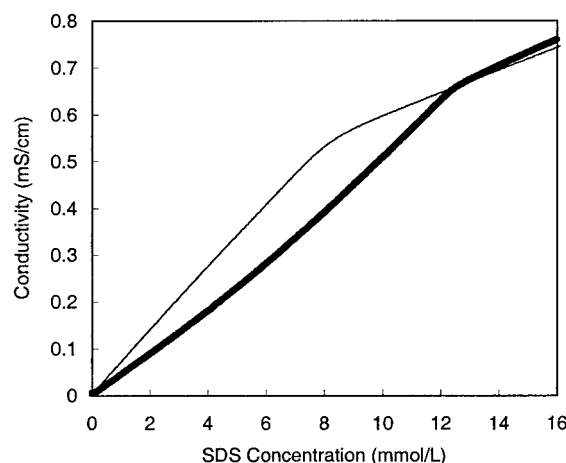


Figure 1 Conductometric SDS titration of distilled deionized water (thin lines) and a cleaned PS latex (thick lines).

TABLE II
Adsorption Densities/Areas at Maximum Packing of SDS for the Cleaned Latices as Determined
by Conductometric Titration

Cleaning period	Latex						
	PS	PBA			PMMA		PMMA'
	14 days	1 day	7 days ^a	> 14 days	7 days ^a	> 14 days	7 days
σ (nm ⁻²)	2.11	1.06	1.35 1.37	1.52	0.77 0.81	0.83	0.84
a_s (Å ²) ^b	47 ± 1	94	74 73	66 ± 3	130 124	120 ± 5	119

^a The two reported values were obtained for independent experiments as shown in Figure 3.

^b The errors were estimated at a 95% confidence level using Student's *t*-distribution for three replicate measurements.

prepared with and without emulsifier, it is concluded that after a period of at least 14 days the surfactant is almost entirely removed from the latex by serum replacement. The respective values of a_s for the three latices are in good agreement with average values cited in literature.^{7,8,12}

When a mixture of two surfactant-free latices is titrated with surfactant, the adsorption density at maximum surfactant packing will depend linearly upon the surface fraction of the compounds in the mixture according to

$$\sigma = f_1\sigma_1 + f_2\sigma_2 = \sigma_2 + f_1(\sigma_1 - \sigma_2) \quad (3)$$

where $f_i = S_{pi}/S_p$ ($i = 1, 2; \sum f_i = 1$) denotes the fractional surface area of latex i of the total polymer/water interface in the blend. This was experimentally verified by Stubbs et al.,⁷ for example. However, if at least one of the latices is not completely free of surfactant, the surfactant molecules will first distribute over the total available polymer surface area at the time of mixing, thus reaching an equilibrium coverage. The influence of surfactant distribution on the adsorption density of the mixed compounds is expressed similarly to eq. (3), for instance,

$$\sigma_i = \sigma_{i0} + f_i(\sigma_{i1} - \sigma_{i0}) \quad (4)$$

where σ_{i0} and σ_{i1} refer to the adsorption densities of compound i in the limits $f_i \rightarrow 0$ and $f_i \rightarrow 1$, respectively. For clarity, this means that a polymer latex i with some residual surfactant will exhibit an adsorption density equal to σ_{i1} when titrated individually, whereas its value will tend to the value σ_{i0} in the presence of a predominant amount of a second latex polymer. In the assumption that the latter compound is surfactant-free, the limiting value σ_{i0} of latex i will then correspond to the adsorption density of its bare surfactant-free surface. The distribution of surfactant upon mixing of latices prior to titration [cf. eq. (4)], has to be incorporated in eq. (3) to fully account for the depen-

dence of the adsorption density at saturation on the composition of the latex blend, for instance,

$$\sigma = \sigma_{21} + f_1(\sigma_0 - 2\sigma_{21}) + f_1^2(\sigma_{11} + \sigma_{21} - \sigma_0) \quad (5)$$

with $\sigma_0 = \sigma_{10} + \sigma_{20}$. In contrast to eq. (3), eq. (5) now predicts a quadratic dependence with respect to f_1 . Note that for a surfactant-free latex blend, $\sigma_{i1} = \sigma_{i0}$ and eq. (5) reduces to eq. (3).

Figures 2 and 3 show plots of σ with respect to the fractional surface area f_1 for different latex blends. Figure 2 refers to a blend of the PS latex cleaned for 14 days, referred to as PS_{14d}, and the PBA latex cleaned for 1 day, referred to as PBA_{1d}. The data clearly reveal a nonlinear dependence which indicates that the surfactant was not completely removed by serum replacement prior to titration. Conversely, a linear relationship does not necessarily mean that the system is

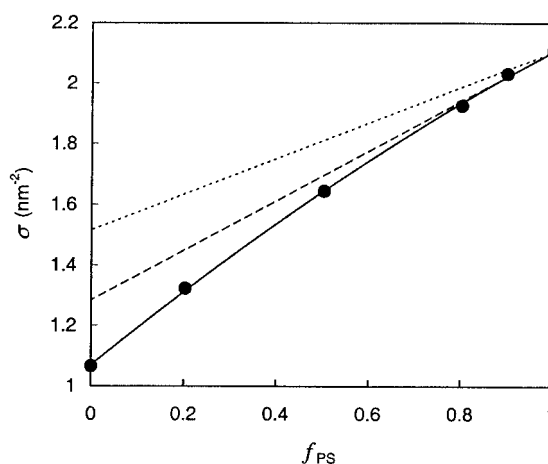


Figure 2 Plot of the saturation adsorption density of SDS as a function of the fractional surface area f_{PS} ($=f_1$) in the binary latex mixture of PS_{14d} and PBA_{1d}. The solid line results from a least-squares comparison of eq. (5) to the data. The dashed line depicts the tangent line of the fitted curve at the value $f_{PS} = 1$. The dotted line represents the expected linear behavior for a surfactant-free latex blend of PS and PBA, as explained in the text.

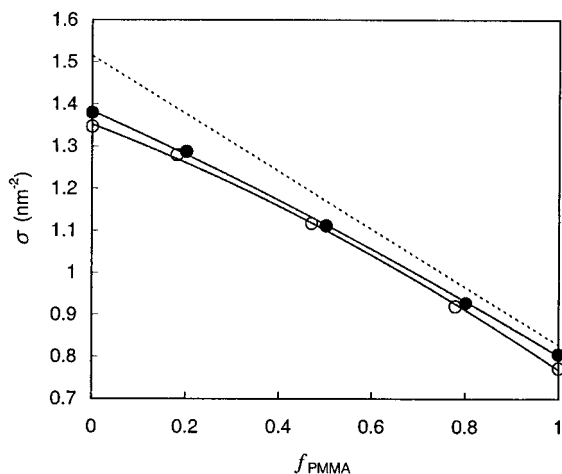


Figure 3 Plot of the saturation adsorption density of SDS as a function of the fractional surface area f_{PMMA} ($=f_1$) in the binary latex mixture of $\text{PMMA}_{7\text{d}}$ and $\text{PBA}_{7\text{d}}$. The open and filled symbols refer to independent experiments. The solid lines result from a least-squares comparison of eq. (5) to the respective data. The dotted line represents the expected linear behavior for a surfactant-free latex blend of PMMA and PBA.

initially surfactant-free because eq. (5) may also be a straight line for the specific condition $\sigma_0 = \sigma_{11} + \sigma_{21}$, where the quadratic term vanishes. The dotted line represents the expected linear trend for blends of surfactant-free PS and PBA latices [eq. (3)] based on the values $\sigma_{\text{S}} = 2.11$ and $\sigma_{\text{BA}} = 1.52 \text{ nm}^{-2}$. A least-squares comparison of eq. (5) to the experimental data set yields the values listed in Table III for the three adjustable parameters σ_0 , σ_{11} , and σ_{21} , with 1 and 2 referring to $\text{PS}_{14\text{d}}$ and $\text{PBA}_{1\text{d}}$, respectively. The resulting quadratic curve is represented by the full line in Figure 2. It is particularly instructive to compare the sums $\sigma_{\text{S}} + \sigma_{\text{BA}}$ (referred to as $\sigma_{1m} + \sigma_{2m}$), $\sigma_{10} + \sigma_{20}$ ($=\sigma_0$), and $\sigma_{11} + \sigma_{21}$ shown in Table III. The following order is found: $\sigma_{\text{S}} + \sigma_{\text{BA}} > \sigma_0 > \sigma_{11} + \sigma_{21}$, which demonstrates that σ_0 is closer to the sum $\sigma_{\text{S}} + \sigma_{\text{BA}}$ of the adsorption densities of the surfactant-free latices than the sum of the individually measured values of the mixed latices, (i.e., $\sigma_{11} + \sigma_{21}$). If one of the latex compounds in the blend is considered as a surfactant-

free reference system, one can approximate σ_{20} from the adjusted parameters as $\sigma_{20} \approx \sigma_0 - \sigma_{11}$, with the underlying assumption that $\sigma_{10} \approx \sigma_{11}$. As mentioned before, σ_{20} can then implicitly be related to the adsorption density of the neat surfactant-free polymer surface of the second compound. It is noticed that $\sigma_0 - \sigma_{11}$ can also be determined from the intercept with the y -axis of the tangent line of the curve at $f_1 = 1$, as depicted by the dashed line in Figure 2. In principle, this can be used to limit the required number of latex blends in the method. However, application of this approach to the present case with $\text{PS}_{14\text{d}}$ as the surfactant-free reference latex shows a disagreement between the values $\sigma_{20} \approx \sigma_0 - \sigma_{11} = 1.28 \text{ nm}^{-2}$ ($a_{\text{s}} = 78 \text{ \AA}^2$) and $\sigma_{\text{BA}} = 1.52 \text{ nm}^{-2}$ ($a_{\text{s}} = 66 \text{ \AA}^2$). This discrepancy is explained by the considerable amount of surfactant present in the $\text{PBA}_{1\text{d}}$ latex, which distributes over the PS latex in the blends, eventually leading to the condition $\sigma_{10} < \sigma_{11}$.

In Figure 3, the latex pair $\text{PMMA}_{7\text{d}}/\text{PBA}_{7\text{d}}$ is considered. The data of two independent experiments (including latex cleaning) are reported. Again, the dotted line represents the expected linear relation for blends of PMMA and PBA latices by using the values $\sigma_{\text{MMA}} = 0.83$ and $\sigma_{\text{BA}} = 1.52 \text{ nm}^{-2}$ for surfactant-free systems. The adjustable parameters σ_0 , σ_{11} , and σ_{21} resulting from a least-squares comparison of eq. (5) to the experimental data sets are given in Table III, with 1 and 2 referring to $\text{PMMA}_{7\text{d}}$ and $\text{PBA}_{7\text{d}}$, respectively. The maximum adsorption density of the PBA surface was estimated from the fit parameters with the $\text{PMMA}_{7\text{d}}$ latex as the reference system. The values $\sigma_{20} \approx \sigma_0 - \sigma_{11} = 1.51$ and 1.47 nm^{-2} were, respectively, found for the independent experiments and here a remarkable agreement is obtained with the value $\sigma_{\text{BA}} = 1.52 \text{ nm}^{-2}$, even in the consideration that the used PMMA latex could contain traces of surfactant. Serum replacement of the PBA latex over a period of 7 days appeared as sufficient to satisfy the condition $\sigma_{10} \approx \sigma_{11}$.

CONCLUSION

In this work, the volumetric determination of the saturation adsorption density of surfactant was studied

TABLE III
Results of a Nonlinear Least-Squares Comparison of eq. (5) with the Experimental Data Shown in Figures 2 and 3

	Latex Blend 1/2				
	$\sigma_{11} \text{ (nm}^{-2}\text{)}$	$\sigma_{21} \text{ (nm}^{-2}\text{)}$	$\sigma_0 \text{ (nm}^{-2}\text{)}$	$\sigma_{11} + \sigma_{21} \text{ (nm}^{-2}\text{)}$	$\sigma_{1m} + \sigma_{2m} \text{ (nm}^{-2}\text{)}$
$\text{PS}_{14\text{d}}/\text{PBA}_{1\text{d}}$	2.106 ± 0.006	1.069 ± 0.008	3.39 ± 0.03	3.18	3.63
$\text{PMMA}_{7\text{d}}/\text{PBA}_{7\text{d}}^a$	0.769 ± 0.008	1.351 ± 0.008	2.28 ± 0.03	2.12	2.35
$\text{PMMA}_{7\text{d}}/\text{PBA}_{7\text{d}}^b$	0.802 ± 0.006	1.383 ± 0.006	2.27 ± 0.03	2.19	2.35

^a Open symbols in Fig. 3.

^b Full symbols in Fig. 3.

in binary latex blends. A phenomenological description is included for latex mixtures which are not totally free of surfactant before titration. It appears that a quadratic dependence is predicted for the saturation adsorption density as a function of the fractional surface area of the latex compounds. By using conductometric titration, the predicted dependence could be verified experimentally in mixtures of homopolymer latices cleaned by serum replacement. This suggests a new approach to control the level of cleaning of the mixed compounds. In addition, it was shown that a fair approximation of the surfactant adsorption area of the bare polymer surface for an incompletely cleaned latex can be obtained from the quadratic curve, in particular, when titrations are carried out with a surfactant-free reference latex.

Full desorption of surfactant adsorbed onto polymer colloids is known to be a lengthy procedure when serum replacement or similar techniques are used. Mixing with an excess of surfactant-free latex will completely desorb the residual surfactant from a partially cleaned latex, the chemical potential acting as

the driving force. This forms the basis behind the approach presented here.

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